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## ABSTRACT

The primary mission of the Reduced Enrichment in Research and Test Reactors (RERTR) Program is to facilitate the conversion of research and test-reactor fuel and targets from high-enriched uranium (HEU) to low-enriched uranium (LEU). One of the current goals at Argonne National Laboratory (ANL) is to assist the Argentine Comisión Nacional de Energía Atómica (CNEA) in developing an LEU foil target and a process for $^{99}$Mo production. Specifically addressed in this paper is ANL R&D related to this conversion: (1) designing a prototype production vessel for digesting irradiated LEU foils in alkaline solutions and (2) developing a new digestion method to address all issues related to HEU to LEU conversion.

## 1. Introduction

Technetium-99m, the daughter of $^{99}$Mo, is the most commonly used medical radioisotope in the world. A number of current producers dissolve/digest uranium-aluminide/aluminum-dispersion plates in alkaline solution as an initial step to recovering fission-product $^{99}$Mo from irradiated high-enriched uranium (HEU). These producers include Institut National des Radioéléments (IRE), Mallinckrodt, and the South African Nuclear Energy Corporation Limited (NECSA). The Argentine Comisión Nacional de Energía Atómica (CNEA) recently converted to using an LEU-Al dispersion target [1]. After irradiation, the $^{99}$Mo is recovered from the irradiated uranium and purified.

To yield equivalent amounts of $^{99}$Mo, an LEU target must contain approximately five times the uranium of an HEU target. Consequently, substituting LEU for HEU requires changes in both target design and chemical processing. Three major challenges have been identified in the substitution of LEU for HEU: (1) modifying the targets and purification processes as little as possible, (2) assuring continued high yield and purity of the $^{99}$Mo product, and (3) limiting economic disadvantages.

The CNEA process has been described in the literature [2] and has much in common with the Mallinckrodt process; both processes are based on that developed by Sameh [3]. In this process, the irradiated targets are heated in sodium hydroxide solution. The aluminum cladding and meat in the targets are dissolved to form sodium aluminate, and the uranium is digested, forming a mixture of $UO_2$ and $Na_2U_2O_7$. The digestion should be done in about 2 L of 1.8-2.0 M NaOH solution to provide enough sodium hydroxide and volume to keep aluminum in solution. If the volume is smaller or less hydroxide is used, aluminum hydroxide will precipitate, clogging the filter and preventing removal of the solution from the digester. Molybdenum is soluble in

alkaline solutions as the molybdate ion, but the actinides and many of the metallic fission products precipitate as hydroxide salts. Following filtration of the dissolver solution, the filtrate is fed into an anion-exchange column, which retains molybdenum and some other anionic species. A series of separation processes purifies the molybdenum to meet pharmaceutical standards.

We have developed LEU metal foil targets that are wrapped in a thin aluminum-foil fission recoil barrier. The foil is held between two aluminum tubes that have been swaged for good thermal contact and welded closed at each end [4, 5]. The fission recoil barrier is present to avoid interaction between the uranium foil and the material of the target, allowing the foil to be removed from the target before digestion. The aluminum mass to be digested for these targets is significantly lower than for the HEU targets currently used by CNEA. Therefore, the LEU foil target can be digested in less than 400 mL of the alkaline solution, which results in a substantial decrease in the amount of liquid radioactive waste.

Early in 1999, Argonne National Laboratory (ANL) began active cooperation with CNEA, with the goal of assisting CNEA to convert to LEU within a few years. Recently, LEU-$Al_x$ dipersion targets have been produced and used in production by CNEA. However, use of this type of target limits CNEA's $^{99}$Mo production capacity to its current level. The volume of liquid waste is equivalent to that produced in the HEU process. In contrast, the LEU-foil process generates very low volume liquid, which can make LEU foil targets superior to the HEU or LEU-$Al_x$ dispersion targets.

## 2. Progress

Since reporting R&D results at the 2002 International RERTR Meeting [6], we have made progress aimed at the conversion of $^{99}$Mo production to LEU targets in two areas: (1) developing a production dissolver and (2) modifying the process for digesting irradiated LEU foils by alkaline solution. Each of these is discussed below.

Prototype Dissolver for CNEA Production

ANL had fabricated a stainless steel vessel for digesting up to 70 g of uranium foil using alkaline solutions. The digester was designed to operate at temperatures up to 300°C and at pressures up to 1100 psig. Further design criteria were: corrosion resistance to gaseous oxygen, maximum overall height of ~50 cm, and easy operation with manipulators in CNEA's hot cells. The vessel was heated by a ceramic beaded heater wrapped around the body of the digester. A shroud fits over the digester body and is useful for directing air during the cool-down operation. The heat-up time is about 30 minutes and the cool-down time is about 60 minutes. The digester has two stainless steel ball valves—one at the bottom for draining material, and one on a tube on the body for feeding liquids or gases, and for venting gases from the digester. When the digester is closed, the bayonet-style cap is lowered onto the digester with a manual screw and twisted to lock the cap. A Viton O-ring is used as a gasket to contain the pressure generated during target digestion, and is replaced with each use of the digester.
A number of operational problems were observed during the digestion tests. A design review was conducted at ANL to discuss the problems. A list of the issues discussed at that meeting follows.

- Four hundred mL of digester solution does not completely submerge a full-sized foil. This is important because a fully submerged target should be digested at a faster rate, and will ensure complete reaction of the foil.
- After many experiments the lower valve began to leak during experimentation. The current valve uses a high-temperature polymer (PEEK) in its sealing surfaces that is rated to 230ºC. Since the process was run at ~280ºC, the temperature rating of the valve was exceeded. We obtained a stainless steel valve that is rated to 450ºC and 1000 psi. This valve is made entirely of metal, with no polymeric parts to degrade, but is very difficult to use in a shielded cell because it requires a significant amount of force to actuate.
- To open and close the digester top, the mechanism was a manual screw that raises and lowers the cap over the O-ring sealing surface. We were concerned that the amount of force needed to pass the O-ring was more than a manipulator could provide.
- The quick-connect fittings on the tubes protruding from the top of the digester have become plugged and very difficult to attach and operate.
- There was repeated failure of pressure gauges attached to the digester. This may be from vapor condensing inside the gauge, and exceeding the rated temperature of the gauge.
- The slurry generated during digestion plugged the lower valve on several occasions, requiring a rod to stir the plug inside and drain the digester

After the design review meeting, we made the decision to purchase a new digester from a commercial vendor. One such commercial vessel is built by Berghof™, and is rated to 250ºC and 3600 psig (Fig 1).

Figure 1. The Berghof™ pressure vessel.

The reactor is sealed by means of two knobs that require only a force equivalent to hand-tightening. The vessel has a replaceable PTFE liner that acts as a seal as well as a chemically inert container.

The vessel has been customized to meet the digestion process requirements: (1) the whole vessel is made of stainless steel 316 Ti (the PTFE liner has been removed), (2) the vessel has been rated up to $T_{max}$=300ºC and $P_{max}$=3600 psig (250 bar), (3) a 3/8-in. dip tube (to the bottom of the vessel) was added in order to evacuate the liquid and the solids without removing the lid, (4) a ¼-in. port for adding liquids was placed in the cap, and (5) a thermocouple well was added to the cap.

The vessel is heated by an electric heating mantle wrapped around the body of the digester. A shroud fits over the digester body and serves as a stand and for directing air during the cool-down operation.

The customized Berghof™ vessel has been used for the experimental tests at ANL.

Process Modification

The original HEU-$Al_x$ process schematic is presented in Figure 2.

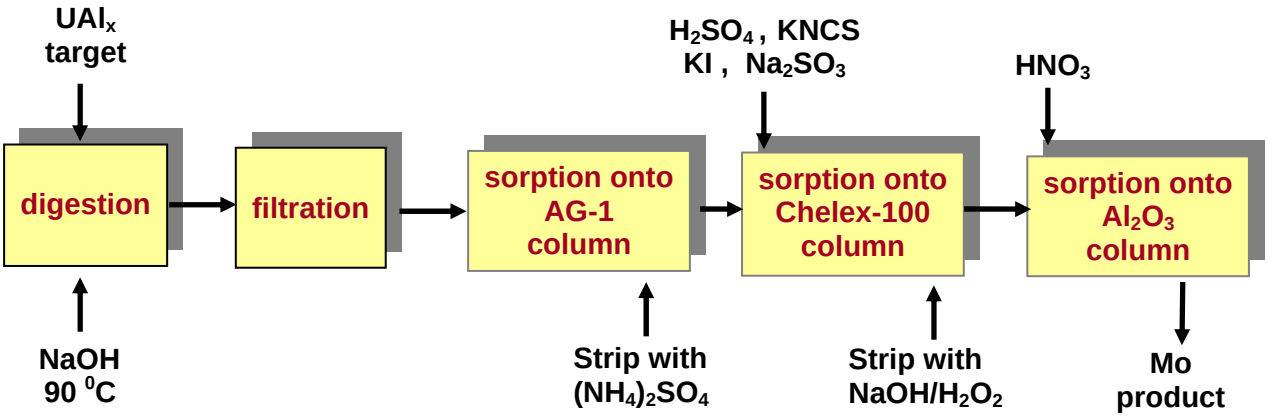


Figure 2. The CNEA HEU process schematic.

The uranium aluminide target with Al cladding is digested in 1.8 M NaOH at 90ºC and filtered. Then the alkaline filtrate containing $^{99}MoO_4^{2-}$ anions is fed onto a column with AG-1 anion exchange resin. After several purification steps, including sorption of Mo(III) thiocyanide complex onto Chelex-100 column and Mo sorption onto alumina column from nitric acid media, a $^{99}$Mo product of the required radiochemical and chemical purity is obtained.

The LEU-modified process began with a $NaOH/O_2$ two-step digestion of LEU foils [6]. An irradiated LEU foil with a 40-µm aluminum fission recoil barrier was processed to recover $^{99}$Mo using the alkaline digestion process and a slightly modified anion exchange process. The foil was loaded into the digester. The atmosphere inside the dissolver was evacuated, and sodium hydroxide solution was injected. The dissolver was then heated to dissolve the aluminum barrier and to convert the uranium foil into a solid uranium oxide product. Following digestion of the

foil and Al barrier in 1.8 M NaOH at about 180ºC and 700 psig (4.8 MPa) hydrogen generated during digestion was evacuated and 85 psig $O_2$ (0.59 MPa) was added to the digester for oxidation of $UO_2$. (It was described earlier that oxidation of $UO_2$ to $Na_2U_2O_7$ was required to get high $^{99}$Mo yield.)

The following equations seemed to adequately describe the chemical reactions of the process:

The first step

$$Al + 3\ H_2O \Leftrightarrow Al(OH)_3 + 3/2\ H_2 \quad (1)$$

$$U + 2\ H_2O \Leftrightarrow UO_2 + 2\ H_2 \quad (2)$$

and the second step

$$UO_2 + 1/2\ O_2 + NaOH \Leftrightarrow 1/2\ Na_2U_2O_7 + 1/2\ H_2O \quad (3)$$

The $^{99}$Mo recovery was 93-95%. The digestion of LEU metal foils generated about 200 mL of the solution. Therefore, the sizes of the primary Bio-Rad AG MP-1 (a macroporous version of AG-1 resin) and Chelex-100 columns were significantly smaller than for the HEU process. This advantage creates far less liquid waste and cuts purification process time considerably; however, development was required to downsize equipment and specify process conditions.

This two-step process is effective but (a) having two warm-up, reaction, and cool-down periods doubles digestion time and (b) using pressurized oxygen leads to safety concerns. Therefore, we are investigating the use of an oxidizing agent to perform the U foil digestion in one step. The oxidizing agent of choice should (1) be highly soluble in alkaline media, (2) not affect the downstream purification process and (3) be readily available. Potassium permanganate has been chosen for this purpose. It reacts with U according to Reaction 4.

$$U + 2KMnO_4 + 2H_2O \Leftrightarrow UO_2(OH)_2 + 2MnO_2 + 2KOH \quad (4)$$

A series of "cold" tests using depleted uranium (DU) foil were conducted at ANL. Adding potassium permanganate converts most of the uranium into the U(VI) hydroxides. However, hydrogen gas generated in the digester from the reactions of Al and U with water (Reactions 1 and 2) can react with permanganate ions by the following reaction:

$$2MnO_4^- + H_2 + 2OH^- \Leftrightarrow 2MnO_4^{2-} + 2H_2O \quad (5)$$

The product of Reaction 5, $MnO_4^{2-}$, is reduced by hydrogen gas, resulting in a formation of $MnO_2$ [7]. The amount of potassium permanganate added to the digester has to be high enough to react with both uranium foil and hydrogen gas. Otherwise, uranium foil digestion and molybdenum release into the solution phase may not be complete.

If the appropriate amount of potassium permanganate is used, the oxidation of uranium foil can be performed in one step, without the use of oxygen gas. This process is shorter and potentially less hazardous than the two-step process with $O_2$ gas. A second benefit of using $KMnO_4$ is that the digestion can be done at a lower sodium hydroxide concentration. As discussed above, 1.8-2.0 M NaOH should be used to form sodium aluminate to avoid the precipitation of aluminum hydroxide, which clogs the filter. According to the literature, manganese dioxide, a product of potassium permanganate's reduction, makes a solid solution with aluminum hydroxide [8]. Experiments performed at ANL demonstrated that a mixed Mn and Al oxide phase does not clog

the filter, and the digestion solution containing $^{99}$Mo as a molybdate ion can be easily filtered. Therefore, there is no need to have a high concentration of NaOH, and 0.5 M NaOH solution can be efficiently used for digestion. This results in much higher uptake of molybdate ion on the AG MP-1 anion exchanger, utilized as the first purification step of $^{99}$Mo from the other fission products [6].

Potassium permanganate's solubility at room temperature is limited: ~0.4 M in $H_2O$ and ~0.35 M in 0.5 M NaOH. The solubility goes up as the temperature increases. If one 35-g LEU foil (~6.9 g $^{235}$U) is digested, hot $KMnO_4$/NaOH solution must be added to the digester to provide enough permanganate.

Three different digestion procedures are being investigated. They have been tested at ANL with low-burnup ($10^{-5}$%) uranium foils prior to the tests with fully irradiated targets in Argentina (Table 1). The targets consist of depleted uranium foil with less than 0.5% $^{235}$U. Weighed DU foils were wrapped in 0.04 mm Al foil of high purity and placed in the two Al capsules. The capsules were welded shut to avoid escape of the fission gases. After two hours of irradiation in a neutron flux of about $10^{13}$ neutrons/cm$^2$·sec and 24 hours of cooling time, both target capsules were cut open. The irradiated DU foils wrapped with Al foil were removed from the inner capsule and digested according to one of the procedures from Table 1. After heating and cooling cycles, the suspension from the digester was transferred through a deep tube into a side-arm flask under vacuum. Then the digester was washed with 100 mL of NaOH solution, and the wash solution was combined with the suspension and filtered through a Whatman™ filter paper. The filtered sludge was placed back into the digester and dissolved in ~3 M $HNO_3$.

Process A (Table 1) is a one-step digestion using solid $KMnO_4$ loaded in the digester after the target is placed there. The digester is evacuated and 400 mL of 0.5 M NaOH is added to the digester. Process B is a one-step digestion using 400 mL of pre-dissolved $KMnO_4$ solution in 0.5 M NaOH. Process C is two-step digestion with 300 mL $KMnO_4$/0.5 M NaOH solution used for the first digestion step. As the second step, the digester is vented to release $H_2$ and fission gases, and $O_2$ gas is added. Thus, large amounts of U, up to 70 g LEU (~14 g $^{235}$U), could be digested, with the total volume of feed to the first ion-exchange column being less than 400 mL, including the volume of the rinse solutions. Process D is similar to the process used at IRE. It was performed to explore the possibility of using 3M NaOH/4 M $NaNO_3$ for the digestion of the LEU foil and to compare the results obtained with those from the suggested A, B and C procedures.

Table 1. Experimental conditions and results for the digestion of the DU-irradiated targets at ANL.

| Process | **A** | **B** | **C** | **D** |
|---|---|---|---|---|
| Description | 1-step solid $KMnO_4$ | 1-step dissolved $KMnO_4$ | 2-step $MnO_4^-/O_2$ Step 1: dissolved $KMnO_4$ Step 2: $O_2$ (100 psig) | 1-step 3M NaOH/4 M $NaNO_3$ (IRE process) |
| DU weight, g | 21.68 | 22.07 | 21.43 | 21.82 |
| Al weight, g | 2.33 | 2.21 | 2.30 | 1.94 |
| $KMnO_4$ weight, g | 44 | 43.5 | 9.48 g for 1st step | - |
| Solution volume, mL | 400 | 400 | 300 | 400 |
| [NaOH], M | 0.5 | 0.5 | 0.5 | 3 |
| $T_{max}$, ºC | 285 ± 5 | 288 ± 5 | 1st 200 ± 5<br>2nd 285 ± 5 | 285 ± 5 |
| Time at max. temperature, min | 30 | 30 | 1st 5<br>2nd 30 | 30 |
| $P_{max}$, psi* | 1300 | 1400 | 1st 100<br>2nd 1000 | 800 |
| $^{99}$Mo recovery, % † | **93** | **99** | **93** | **97** |

* 1 psi ~ 7 kPa

† Estimated standard deviation is about 3%

The digestion results for the DU-irradiated targets are presented in Table 1. The recovery of $^{99}$Mo was calculated as follows. The $^{99}$Mo activity in the alkaline filtrate was determined by gamma counting at 181.1, 739.4 and 777.8 keV. To determine an amount of Mo remaining in the solid phase, the whole sludge was dissolved in ~3 M $HNO_3$, stable Mo was added to the solution, and alpha-benzoin oxime was added to precipitate Mo. The suspension was filtered; the precipitate was washed with 1 M $HNO_3$ and then digested in 0.2 M NaOH/1% $H_2O_2$. The solution was analyzed by gamma counting for $^{99}$Mo content. The $^{99}$Mo recovery was calculated as a ratio of the $^{99}$Mo activity in the alkaline filtrate product to the sum of the $^{99}$Mo activity in the alkaline filtrate and in the digested alpha-benzoin oxime solution.

Table 2. Procedures for digestion of the irradiated targets at ANL

| Process | **A** | **B** | **C** | **D** |
|---|---|---|---|---|
| Description | 1-step solid $KMnO_4$ | 1-step dissolved $KMnO_4$ | 2-step $MnO_4^-/O_2$ Step 1: dissolved $KMnO_4$ Step 2: $O_2$ | 1-step 3M NaOH/4 M $NaNO_3$ (IRE process) |
| Advantages | • No $O_2$ gas addition required<br>• Digestion takes less than half as long as 2-step digestions<br>• $KMnO_4$ addition allows use of lower $[OH^-]$, therefore more efficient Mo recovery in ion exchange | • No $O_2$ gas addition required<br>• $KMnO_4$ addition allows use of lower $[OH^-]$, therefore more efficient Mo recovery in ion exchange | • Feed volume is not set by $KMnO_4$ addition, therefore lower than process A<br>• $KMnO_4$ addition allows use of lower $[OH^-]$, therefore, more efficient Mo recovery in ion exchange | • Less solid waste than A, B and C |
| Disadvan-tages | • Generates greater amount of solid uranium waste due to the presence of $MnO_2$ | • Generates greater amount of solid uranium waste due to the presence of $MnO_2$<br>• Hot saturated $KMnO_4$ solution must be added into digester | • Generates greater amount of solid uranium waste due to the presence of $MnO_2$<br>• Digestion takes more than twice as long as 1-step digestions | • Solution is hard to filter<br>• $NO_3^-$ prevents using anion exchange for $MoO_4^{2-}$ recovery in downstream process |

Successful $^{99}$Mo recovery was obtained for all four procedures. Processes A, B, and D have the shortest process time – 1 hour heating and 1 hour cooling (to 90ºC), while total process time for Process C is more than 3 hours (Table 2). Process D has the lowest amount of solid waste. However, the alkaline filtrate, containing $^{99}$Mo, must be acidified prior to the purification steps due to the presence of the nitrate anions. High $NO_3^-$ concentration makes the molybdate sorption in alkaline media very ineffective.

The use of permanganate in Process C eliminates the problem with $Al(OH)_3$ precipitation and consequent clogging of the filter. If $O_2$ gas is used for the second step, large amounts of U, up to 70 g LEU (~14 g $^{235}$U), could be digested without significant increase in the amount of solid and liquid waste.

Processes A and B are simple and cost-effective processes, providing high $^{99}$Mo recovery.

For all the tested procedures some black $UO_2$ was observed in the sludge, indicating incomplete oxidation of U metal to U(VI). Most likely, the oxidizing agents react simultaneously with both Mo and the target material, e.g. U, fission products and—in the case of Processes A, B and D—with $H_2$ gas, produced by Reactions 1 and 2. Our previous data [9] and the new data for Mo recovery using Process B, reported in this paper, are shown in Figure 4.

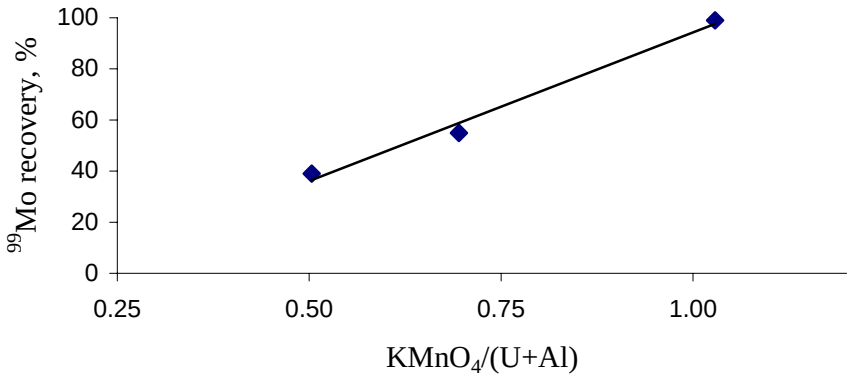


Figure 4. Molybdenum recovery from Process B as a function of the ratio of $KMnO_4$ to U and Al, expressed in molar equivalents.

Figure 4 demonstrates that Mo recovery increases if the amount of permanganate increases. If the total amount of molar equivalents of $KMnO_4$ is equal to the sum of the molar equivalents of U and Al, 99% $^{99}$Mo recovery could be achieved.

## 3. Future Work

We plan to discuss our results with CNEA to determine the best and most effective process for digestion of the irradiated LEU foil targets in Argentina. At ANL, we will continue study of the $^{99}$Mo purification steps and optimization of the digestion process and waste removal and minimization.

## 4. Conclusions

- A commercial Berghof™ vessel was customized and purchased by ANL. This vessel has been successfully used at ANL for the digestion tests of irradiated and non-irradiated uranium foils
- Four digestion/oxidation methods are currently being investigated. All four methods have been used on irradiated low-burnup targets at ANL. Recovery of $^{99}$Mo has been >90% for each process.
- In consultation from CNEA, future work will address the existing uncertainties and will optimize the process for use in CNEA's hot cell facilities

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